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COMPLETE SPECIFICATION.

Recovery of Crude Hecogenin from Agave Leaves.

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The present invention concerns the hydrolysis of heconin obtained from agave leaves and the recovery of the resulting crude hecogenin.

The product of the process according to the invention which is referred to herein as "crude hecogenin" contains less than 95% and as a rule between 10—70% by weight of pure hecogenin.

It is known that heconin is contained in the juice of agave leaves and that this juice can be submitted to suitable hydrolysis treatment for the recovery of hecogenin.

While the starting material has always a water content at least sufficient for the hydrolysis of the heconin, its natural acidity, as a rule between 4 and 5, is insufficient for hydrolysis under normal pressure and therefore in conventional processes for the production of hecogenin from agave leaves the starting material is admixed with considerable quantities of an acid such as sulphuric acid, and the reaction mixture is boiled under normal pressure. The quantities of the added acid are as a rule quite substantial, in particular where the concentration of the heconin in the starting material is low. The need to use high quantities of acid in the known process affects the price of the final product, both because of the acid consumption itself and because of the ensuing complication of the working-up procedure.

Accordingly, a further process was developed in which the agave juice serving as starting material is first submitted to autolysis. During this autolysis the juice separates into a slurry and a supernatant, substantially clear liquor. The latter is removed and the slurry is then submitted to hydrolysis under pressure at a temperature ranging between 140° and 250° C. for example, as described in British Specification No. 797,384.

The autolysis of the juice has the disadvantage that the further it progresses the slower becomes its rate. After 3—4 days the rate of autolysis becomes as a rule so low that for practical considerations the process has to be interrupted. However, as a result of this interruption a considerable proportion of the heconin present in the starting juice does not enter the final hydrolysis step and is lost. This loss constitutes an obvious disadvantage.

It is accordingly the object of the present invention to provide an improved process for the production of crude hecogenin from the agave juice.

The invention consists in a process for the production of crude hecogenin from the juice of agave leaves, wherein the juice is submitted to acidic hydrolysis under pressure at a temperature exceeding 100° C. and the precipitate that forms containing the crude hecogenin is separated and treated with an aqueous alkali solution.

In one embodiment of the invention acid is added to the juice in an amount of up to 10% by weight of the juice.

If desired the purification with an aqueous alkali may be preceded by an extraction of the product of hydrolysis with an alcoholic

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acid solution and recovery of the extracted crude hecogenin from the resulting extract.

By the treatment of the hydrolysate with alkali impurities are removed. Functionally this treatment comes instead of the autolysis in the known process and has the advantage of achieving substantially the same result in a much faster and more convenient way. The treatment with alkali can consist in mere washing or also in slurrying the hydrolysate in an aqueous alkaline solution and then again separating the precipitate. This may, if desired, be repeated several times.

The juice serving as starting material may be the natural juice squeezed out of agave leaves, or a previously concentrated product. Preliminary concentration of a juice may, for example, be effected by any of the methods described in British Patent Specification No. 957,655. The juice may also be predominantly freed of undesired matter by treatment with calcium hydroxide or carbonate.

Depending on the applied pressure and the natural acidity of the starting material it is possible either to do without the addition of any acid or with such quantities of added acid which, compared with the quantities required in conventional processes, are very small.

Where the process according to the invention is carried out continuously, the starting material, if desired after admixture of a certain amount of acid, is fed continuously, under pressure, into a sealed reaction vessel in which the temperature is maintained at at least 150° C. From the reaction vessel the mixture is discharged continuously and the precipitated aglycones are filtered off and submitted to the treatment with aqueous alkali, as specified. The residence time in the reaction vessel depends on the time of reaction which in its turn depends on the *p*H of the mixture and the temperature and pressure at which the reaction proceeds.

The aglycones produced in accordance with the invention constitute the desired crude hecogenin whose pure hecogenin content is usually comprised between 10 and 95% by weight, depending on the nature of the starting material.

The invention is illustrated by the following Examples without being limited thereto.

EXAMPLE 1.

10 litres of juice from the leaves of an 8-year old agave was heated to 95° C. The precipitate formed was filtered off after prior decantation of a portion of the supernatant mother liquor. The filtrate was mixed with 1kg. of a 60% sulphuric acid and heated under pressure at 145° C. for 1 hour in an autoclave. The mixture was cooled to 90° C. and filtered through linen. The precipitate obtained was transferred to a 2-litre flask provided with a reflux condenser and containing 1 litre of a 20% sulphuric acid. The resulting mixture was refluxed for 3 hours and then filtered while hot. In this manner residual glycosides were hydrolysed. The filter residue was washed first with water, then with a 1% aqueous soda solution, and again with water and dried at 110° C. 89.5 g. of a brown powder containing 13.8 g. of hecogenin was obtained.

EXAMPLE 2.

Agave juice as in Example 1 was heated under pressure and without addition of acid (the natural *p*H being 4.5) for 3 hours at 220° C., thereafter cooled and filtered through linen. The filter cake thus obtained was dispersed in 0.5 litre of a 15% by weight methanolic sulphuric acid, 2 g. of activated charcoal was added to the dispersion and the mixture refluxed while stirring for 3 hours. Thereafter the hot mixture was pressed through linen, the filtrate cooled and admixed while stirring with 1 g. of activated charcoal and so much water as to form a 70% alcoholic solution. A yellowish-brown precipitate mixed with carbon was filtered off, washed successively with water and a 5% ammonia solution and dried. The yield of crude hecogenin was 0.14% by weight of the starting juice and it contained 67.2% of pure hecogenin.

EXAMPLE 3.

2 litres of juice from agave leaves was neutralized with calcium carbonate to *p*H of about 7.0 and heated to the boil. The precipitate which formed was left to settle, the liquid separated by decantation and filtration and mixed with 95 g. of a 60% by weight sulphuric acid (final acid concentration 2.5%). The sulphuric acid-juice mixture was pumped through a stainless-steel pipe by means of two gear-pumps, each near one end of the pipe so that the pressure prevailing inside the pipe was controlled by the rate of pumping. The rate of pumping and the length of the pipe were so selected that the reaction mixture remained in the reaction zone of the pipe for 10 minutes, the temperature of which zone was kept at 180° C. Ten minutes after all of the juice was pumepd into the pipe, the apparatus was cooled and any residual reaction mixture remaining in the pumps and pipe recovered. The precipitate was filtered off, washed with water, a 2% by weight aqueous sodium hydroxide solution and again with water. Altogether 3.95 g. of crude hecogenin containing 2.02 g. of pure hecogenin was obtained.

EXAMPLE 4.

Agave leaves were squeezed out yielding 14 kg. of juice. The *p*H of the juice was

raised to 8 by the addition of calcium hydroxide. The juice was then heated until coagulation took place and the precipitate was separated by centrifugation. After drying in vacuo 270 g. of a green powder was obtained. The filtrate was acidified with H_2SO_4 to *p*H3, charged into autoclave and heated at 160° C. for 60 minutes. The precipitate formed was easily filtered off, washed first with water and thereafter with an aqueous 5% HN_4OH solution. After drying 106 g. of a light brown powder was obtained, containing 29.6 g. of hecogenin.

EXAMPLE 5.

6 litres of agave juice of *p*H 4.80 (natural) was heated under pressure at 160° C. for 3 hours and the precipitate formed filtered off, washed with water and dried. 1576 g. of a brown powder was thus obtained. This product was boiled with two portions of a 10% aqueous soda solution, each boiling being followed by centrifugation. The hydrolysate was then washed with water and dried and in this manner there was obtained 98 g. of a product that contained about 14% of hecogenin. The alkaline filtrates were accumulated and acidified to *p*H2 whereupon a precipitate formed. After separation, washing and drying, 58 g. of a dark brown powder was obtained which did not contain any hecogenin.

EXAMPLE 6.

8.1 litres of agave juice was acidified with H_2SO_4 to *p*H3 and heated under pressure to 160° C. for 20 minutes. The precipitate which formed was filtered off, washed with a hot 5% aqueous soda solution and water and dried at 110° C. 94 g. of a grey green powder containing about 16 g. hecogenin was obtained. The alkaline filtrates gave on precipitation, as in Example 5, 19.5 g. of a dark brown powder that contained no hecogenin.

WHAT WE CLAIM IS:—

1. A process for the production of crude hecogenin from the juice of agave leaves, wherein the juice is submitted to acidic hydrolysis under pressure and at a temperature exceeding 100° C., and the precipitate that forms containing the crude hecogenin is separated and treated with an aqueous alkali solution.
2. A process according to Claim 1, wherein the reaction mixture contains up to 10% by weight of added acid.
3. Process according to Claim 2, wherein said added acid is sulphuric acid.
4. Process according to Claim 1, wherein the reaction mixture does not contain any added acid.
5. A process according to any one of Claims 1 to 4, wherein the hydrolysis is effected continuously by passing the reaction mixture in a continuous manner through a suitable reaction vessel in which the temperature is maintained at least 150° C.
6. Process according to any one of the preceding claims, wherein the purification with an aqueous alkali solution is preceeded by an extraction of the product of hydrolysis with an alcoholic acid solution and recovering the crude hecogenin from the resulting extract, for the subsequent treatment with an aqueous alkali solution.
7. Process according to Claim 6, wherein the acid is sulphuric acid.
8. Process for the production of crude hecogenin from juice of agave leaves substantially as hereinbefore described with reference to the Examples.
9. Crude hecogenin when obtained by a process according to any one of Claims 1 to 8.

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